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**The following statements are taken from documents filed by the applicant.**  
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(54) Process for Reducing Nitrogen Oxides and Black Smoke in Exhaust Gases from Diesel Motors and Device for Conducting the Process.

(57) The invention involves a process for reducing nitrogen oxides and black smoke in exhaust gases from diesel motors by injecting water into the combustion chamber of the diesel motor (50), whereby the injected water is obtained from the exhaust gas of the diesel motor (50). According to the invention, water vapor is separated from the exhaust gas stream by a porous membrane (5) into a vapor chamber (4) bounded by the membrane (5) and a cooling surface (7). The water vapor is condensed in the vapor chamber (4).

(Translator's note: The drawing on the first page of the German text is not pertinent to the numbers in the preceding paragraph. See Figure 1 attached for the pertinent diagram with numbered parts. Also, lines are missing from the page bottoms of the German text. The missing text is indicated in this translation by a dotted line like this.....)

## Specification

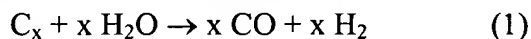
The invention involves a process for reducing nitrogen oxides and black smoke in exhaust gases from diesel motors by injecting water into the combustion chamber of the diesel motor according to the preamble in Claim 1 and a device for conducting the process.

It is known that injecting water into the combustion chamber of diesel motors can be an effective measure to reduce nitrogen oxides and black smoke.

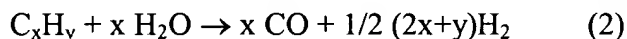
Although the determining processes, which ultimately lead to a reduction in noxious substances by means of these measures, are not at all known in detail, the reduction in nitrogen oxide (essentially NO) seems to result therefrom so that the combustion enthalpy required to vaporize the injected water is diminished, which reduces the combustion temperatures correspondingly. Consequently, on thermodynamic and in particular, reaction kinetics grounds, less nitrogen oxides are produced

Far less clear-cut is the action of the water used relative to the observed minimizing of black smoke. The following possibilities are considered:

i. Carbon particles (1 nm size range) formed by pyrolysis of long-chain hydrocarbons in locally superfatted combustion areas are decomposed by water vapor at high temperatures according to the following reaction:



ii.. Smaller hydrocarbon units (for example, the acetylene  $C_2H_2$  or other material postulated as a carbon black precursor) from the thermal precracking of long-chain hydrocarbons enter into the following reaction with water at high temperatures, skipping a condensed phase:



iii. water vapor is partially split radicalwise at high temperatures (into hydrogen atoms and hydroxyl radicals), the hydroxyl radicals ( $OH^\cdot$ ) oxidize either the first-formed carbon black particles or the already present carbon black precursors.

The processes i) and ii) are preferred over iii), on the basis of thermodynamic facts. The reaction equilibriums for the reforming reactions (1), (2) are quantitatively on the product side starting at ca. 1000 K. In contrast, the equilibrium concentration of OH radicals only achieves at 2500 K values that lead to the expectation of a significant oxidative decomposition of carbon black.

As already described, injecting water into the combustion chamber is associated with a reduction in the average combustion chamber temperature resulting from the vaporization enthalpy to be applied as well as from heating the water vapor to equilibrium temperature. Efficiency losses result because the added water changes the polytropic exponent (ratio of the specific heats) in a manner unfavorable for effective useful work by the expansion.

Reduction of noxious materials is therefore related to an increase in the specific fuel consumption.....the endothermic reforming reactions (1) and (2) and the endothermic process similarly described under iii). Consequently, the quantity of injected water must be limited in the direction of tolerable efficiency losses.

Appropriate motor experiments show that a value of ca. 30 mass percent of injected water, relative to the quantity of injected hydrocarbon, should not be exceeded.

The simplest way to provide water for admixing/injection in a vehicle is a built-in water tank. However, this requires additional space in the vehicle and adds weight. This implementation also proves to be disadvantageous from the standpoint of service station logistics.

Another source for providing water is the exhaust gas. It is already known in the field of H<sub>2</sub> combustion motors (DE 31 02 088) that water required for the motor under certain operating conditions can be obtained on-board by condensation from motor exhaust gases. The exhaust gas of a diesel motor contains, like all exhaust gas from a combustion process, water vapor as a combustion product. The water vapor concentration fluctuates between 3 and 11 percent by volume according to the manner of operation at idling and full load. It is estimated that about a third of the water present in the exhaust gas would suffice for recycling to inject into the motor.

Exhaust gas temperatures can reach values up to 700° C directly at the exhaust gas manifold. However, the dew point of the exhaust gas lies in a temperature range of 40 - 60° C, so that the diesel motor in a typical utility vehicle must recycle water through a cooling area (condensation) having a refrigeration capacity of ca. 50 – 60 kW.

Water to be separated adsorptively from the exhaust gas stream condenses on the basis of the required adsorber volume and the high regeneration temperatures.

Another possibility for obtaining water from the exhaust gas of combustion motors is known from US 4,725,359. Water is separated from the exhaust gas stream by use of a dense solution/diffusion membrane. A vacuum pump is connected on the permeate side to maintain the necessary water partial pressure difference. The water vapor sucked out by the pump is condensed in a separate condenser before or after the vacuum pump. Potable water of high purity is obtained by the use of a hydrophilic dense membrane. However, the disadvantage of the process is the low separation efficiency and the expensive construction of the device associated with the use of a vacuum pump.

The problem involved in the invention is to improve a process for reducing nitrogen oxides and black smoke in exhaust gases from diesel motors by injecting water into the combustion chamber of the diesel motor, the improvement being to provide water in a manner to avoid the disadvantages associated with the process disclosed in US 4,725,359 for separating water from combustion exhaust gases.

This problem is solved by the process according to Claim 1. An advantageous version of the invention's process and a device for performing the process are subjects of additional claims.

According to the invention, a porous membrane is used to separate water vapor from combustion exhaust gases. The water vapor passes through the membrane ..... through and is condensed on a cooling surface. The driving force for the transport of the water vapor through the membrane is, as in US 4,725,359, the water partial pressure difference on both sides of the membrane. The water partial pressure on the permeate side is, however, in the

invention's process, essentially equal to the H<sub>2</sub>O vapor pressure over the condensate film. Consequently, pumping to lessen the water partial pressure on the permeate side is not necessary.

The water vapor is preferably transported convectively through the porous membrane onto the condensate film. Water and the other condensable components in the exhaust gas pass through the membrane. The non-condensable components remain essentially in the exhaust gas stream. Due to convective transport, the water vapor is separated more rapidly than through a dense membrane having a considerably higher transport resistance.

High H<sub>2</sub>O separation efficiency can be achieved with the invention, so that it can be used particularly advantageously for utility vehicles.

Membrane materials primarily having low thermal conductivity can be used. A ceramic membrane, a polymer membrane or a metal-ceramic composition membrane is used advantageously. Examples are Teflon®, ceramic oxide materials, such as, for example, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and metal structures filled with ZrO<sub>2</sub>.

Macroporous membranes are particularly advantageous, preferably having a pore width in the range of 100 nm to 10,000 nm and in particular, in the range of 100 nm and 1000 nm.

The invention is described in more detail by figures. These show:

Figure 1 – the schematic diagram of a membrane module for use in the invention's process;

Figure 2 – the process diagram to reduce nitrogen oxides and black smoke in exhaust gases from diesel motors by injecting water, whereby, according to the invention, the water is separated from the exhaust gas stream;

Figure 3 – the concrete example of a membrane module

Figure 2 shows the process diagram for reducing nitrogen oxides and black smoke in exhaust gases from diesel motors by injecting water, whereby, according to the invention, the water is separated from the exhaust gas stream of a diesel motor **50**. The core of this assembly is the membrane module **10** where the water is separated. This is shown in an enlarged scale in Figure 1. It has the following spatial partitioning:

- Exhaust gas chamber **2** that is bounded by a porous membrane **5**;
- Gas chamber **4**, which is bounded on one side by a porous membrane **5** and on the other side by a heat exchanger plate **7**; in the example shown, membrane **5** and heat exchanger plate **7** run essentially mutually parallel;
- Coolant chamber **6**, which is bounded on one side by the heat exchanger plate **7**.

Exhaust gas from the diesel motor **50** is conducted into the exhaust gas chamber **2** of the membrane module **10**. The water vapor in the exhaust gas stream is separated by the porous membrane **5** in the gas chamber **4**. The gas chamber **4** is joined directly to the membrane side away from the exhaust gas. It is bounded by a cooled heat exchanger plate **7** having a coolant (preferably brine containing glycol) that ..... of the cooled plate **7** condenses the water vapor (condensate film **9**) diffusing through the pores of membrane **5** and the gas chamber **4** and collects it in a condensate trap **54** having a connected buffer storage unit **56**. The water can

be withdrawn from there, for example, by a metering pump 58 directly for injection into the diesel motor 50.

The driving force for the transport of the water vapor through the membrane 5 is generated by the partial pressure difference between the exhaust gas stream in the exhaust gas chamber 2 and the condensate film 9 on the cooled plate 7.

The coolant, with which the heat of the water released on condensation (ca. 0.7 kW/kg water) is drawn off convectively from the membrane module 10, is passed through a conduit 70 and circulated with the aid of a circulation pump 72. The temperature of the coolant must be adjusted so that the required dew point of the exhaust gas stream is reached. A cooling device 74 is located in the cooling circuit to remove the heat absorbed by the coolant.

Besides the demarcations presented by the membrane 5 and the heat exchanger plate 7, the gas chamber 4 can be open to the environment, so that the interior of the gas chamber is at ambient pressure.

Membrane 5 and gas chamber 4 together form a gap between the hot exhaust gas and the condensed water film 9, which has a low thermal conductivity (for example, for Teflon® as the membrane material  $\lambda = 0.23 \text{ W/mK}$  compared to aluminum having a  $\lambda = 200 \text{ W/mK}$  on dehumidification with a surface cooler). Thus, the entire gas stream does not have to be cooled to the appropriate dew point in practicing the invention's process. Due to the higher thermal conductivity by a factor of 1000, the condensation heat is passed in the first place through the heat exchanger plate to the coolant. In the ideal case, only a cooling efficiency corresponding to the condensation heat is required, which leads to a significant energy saving in cooling.

From the standpoint of adequate thermal insulation between the exhaust gas and the condensed water film 9, the space between membrane 5 and heat exchanger plate 7 is selected preferably in the range of ca. 2 to 10 mm.

Deposits of carbon black particles on the exhaust gas side of the membrane can be loosened periodically by back-flushing with compressed air from the on-board compressed air system and carried away with the exhaust gas stream.

Figure 3 shows a concrete embodiment of a membrane module. Several individual membrane modules 10 of Figure 1 are integrated together in a stack. Adjoining membrane modules 10, 10' are positioned here advantageously so that the exhaust gas chamber (2) is bounded on two sides by the porous membrane 5. The gas chambers 4 are joined to the membranes 5 in each case with the heat exchanger plates 7 as the boundary. The heat exchanger plates 7 are in thermal contact with the liquid coolant that is located in the coolant chamber 6. The inlet and outlet for the coolant are indicated by the arrows 30, 32. Arrow 34 indicates the outlet for the condensate 9. Spacers 40 are present in the individual chambers. The entire stack is enclosed by a shell 42. The device as a whole has a plate-shaped construction.

## Patent Claims

1. Process for reducing nitrogen oxides and black smoke in exhaust gases from diesel motors by injecting water into the combustion chamber of the diesel motor (50). characterized in that .....(50) is obtained, whereby water vapor is separated from the exhaust gas stream by a porous membrane (5) in a gas chamber bounded by the membrane (5) and a cooling surface (7), and the water vapor is condensed in the gas chamber (4).

2. Process according to Claim 1, characterized in that a coolant, which is in thermal contact with the cooling surface (7), is passed through a circulation system.

3. Device for conducting the process according to one of the preceding claims, characterized by a porous membrane (5), by means of which water vapor is separated from the exhaust gas stream, a gas chamber (4) bounded by the porous membrane (5) and a cooling surface (7) on which condensation can take place, and a coolant in thermal contact with the cooling surface (7).

4. Device according to Claim 3, characterized in that the pore width in the porous membrane (5) is 100 nm to 10,000 nm, preferably 100 to 1000 nm.

5. Device according to Claim 3 or 4, characterized in that the porous membrane (5) is a ceramic membrane or a polymer membrane or a metal-ceramic composite membrane.

6. Device according to one of Claims 3 to 5, characterized in that the membrane (5) and the cooling surface (7) run essentially parallel to one another at a spacing of 2 to 10 mm.

7. Device according to one of Claims 3 to 6, characterized in that it is constructed as a type of plate module.

24 September 2001

Fig. 1

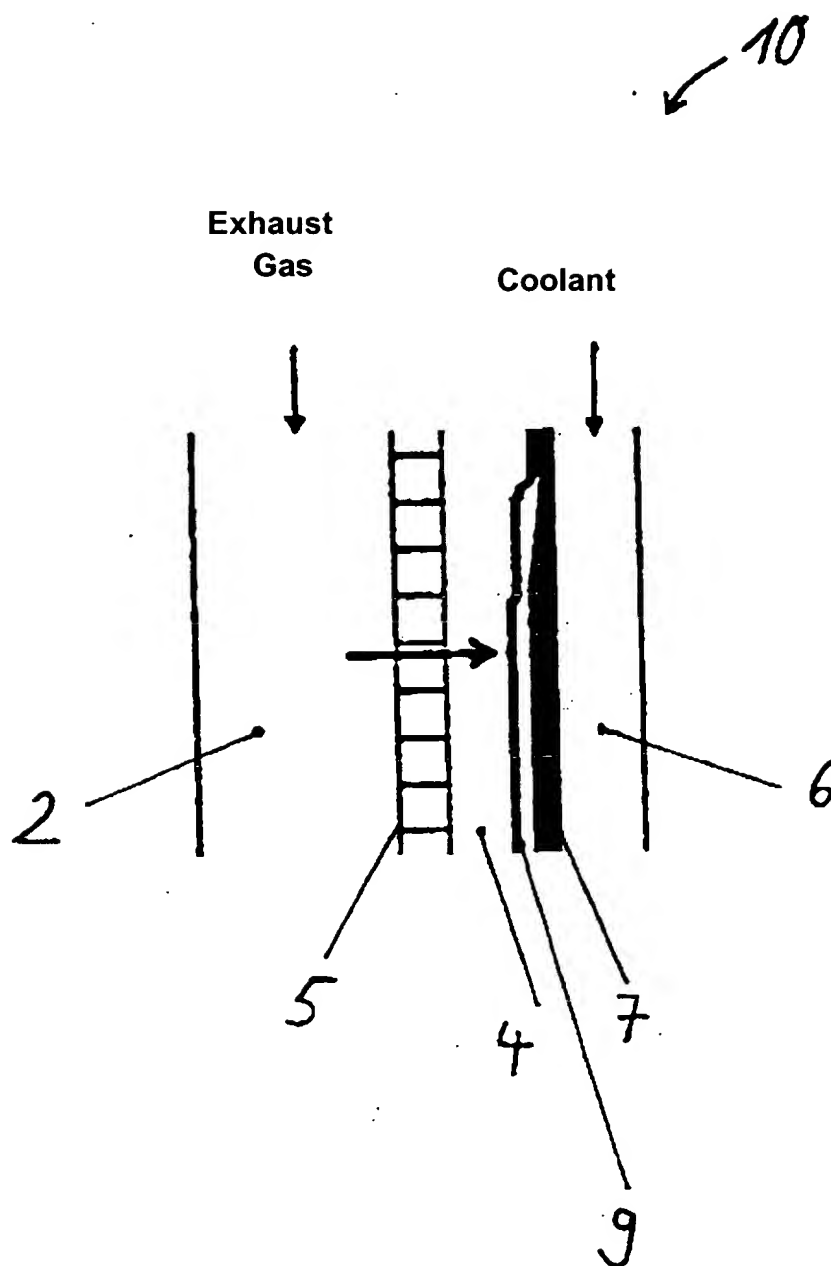


Fig. 2

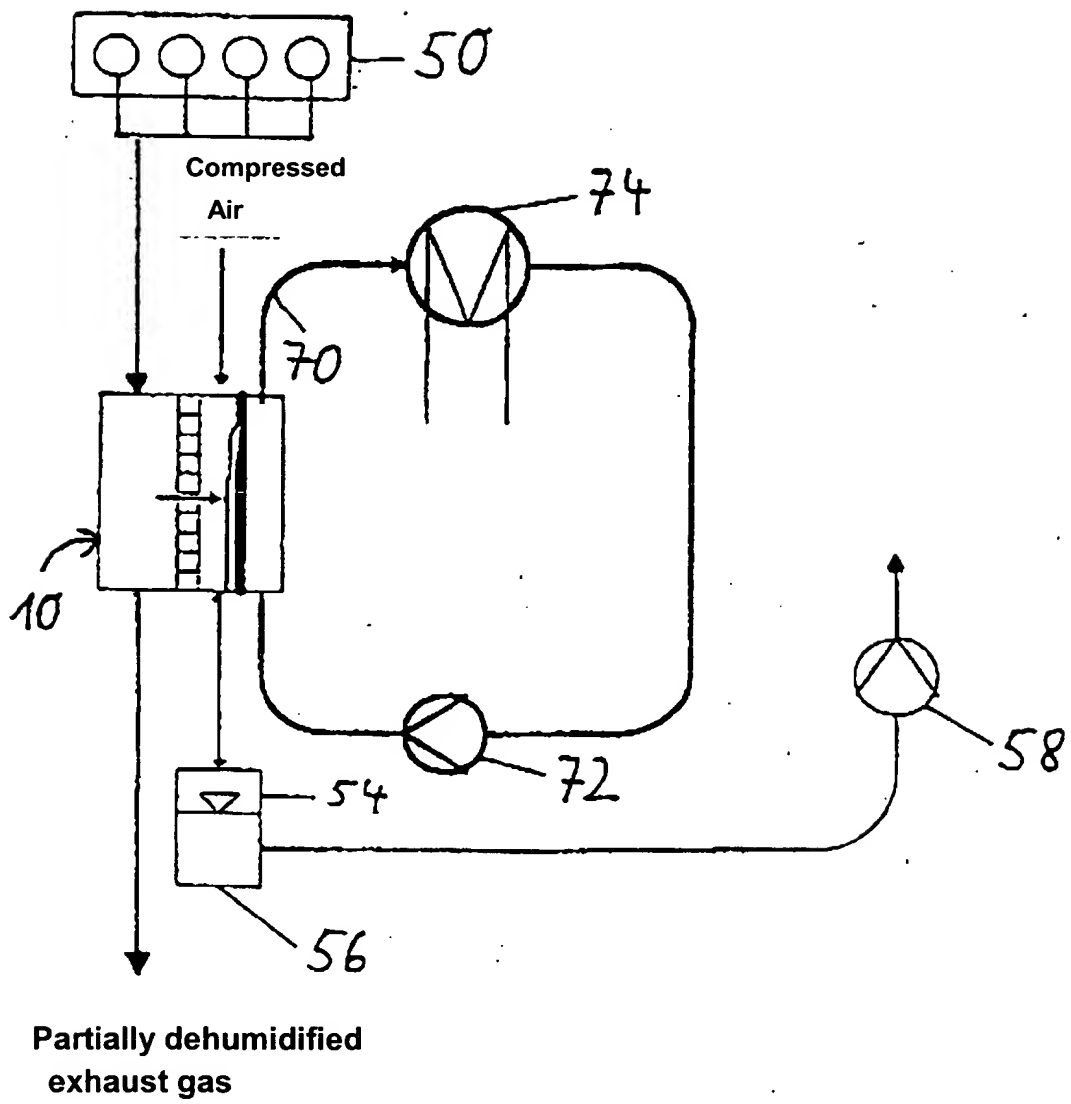


Fig. 3

